

REPORT DOCUMENTATION PAGE				<i>Form Approved</i> OMB No. 0704-0188	
Public reporting burden for this collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing this collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing this burden to Department of Defense, Washington Headquarters Services, Directorate for Information Operations and Reports (0704-0188), 1215 Jefferson Davis Highway, Suite 1204, Arlington, VA 22202-4302. Respondents should be aware that notwithstanding any other provision of law, no person shall be subject to any penalty for failing to comply with a collection of information if it does not display a currently valid OMB control number. PLEASE DO NOT RETURN YOUR FORM TO THE ABOVE ADDRESS.					
1. REPORT DATE (DD-MM-YYYY) 02-03-2012		2. REPORT TYPE Briefing Charts		3. DATES COVERED (From - To)	
4. TITLE AND SUBTITLE Cyanate Ester Graphene Composites				5a. CONTRACT NUMBER	
				5b. GRANT NUMBER	
				5c. PROGRAM ELEMENT NUMBER	
6. AUTHOR(S) Josiah T. Reams, Andrew Guenther, Kevin R. Lamison, and Joseph M. Mabry				5d. PROJECT NUMBER	
				5f. WORK UNIT NUMBER 23030521	
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) Air Force Research Laboratory (AFMC) AFRL/RZSM 9 Antares Roac Edwards AFB CA 93524-7401				8. PERFORMING ORGANIZATION REPORT NUMBER	
9. SPONSORING / MONITORING AGENCY NAME(S) AND ADDRESS(ES) Air Force Research Laboratory (AFMC) AFRL/RZS 5 Pollux Drive Edwards AFB CA 93524-7048				10. SPONSOR/MONITOR'S ACRONYM(S)	
				11. SPONSOR/MONITOR'S NUMBER(S) AFRL-RZ-ED-VG-2012-059	
12. DISTRIBUTION / AVAILABILITY STATEMENT Distribution A: Approved for public release; distribution unlimited. PA# 12175.					
13. SUPPLEMENTARY NOTES For presentation at the 243 rd ACS National Meeting, San Diego, CA, 25-29 March 2012 and publication in Polymer Preprints, March 25, 2012.					
14. ABSTRACT Graphene oxide produced by chemical oxidation formed stable dispersions in LECy cyanate ester matrix and edge functionalized graphite does not. High shear mixing followed by sonication was the best method for graphene oxide dispersion in LECy. Addition of 1 wt% edge-functionalized graphite of LECy did not increase storage modulus but addition of 1 and 2 wt% GO increased storage modulus below the T _g . Diffusion of water in LECy 1 wt% GO was slower than pure LECy polycyanurate but equilibrium uptake was greater. SEM micrographs of composite fractured surfaces suggest that LECy cyanate resin matrix is covalently bonded to graphene oxide sheets. LECy 1 wt% GO composite samples showed relatively good dispersion and low void content. Poor dispersion and large voids were present in LECy 5 wt% composites.					
15. SUBJECT TERMS					
16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT SAR	18. NUMBER OF PAGES 20	19a. NAME OF RESPONSIBLE PERSON Dr. Joseph M. Mabry
a. REPORT Unclassified	b. ABSTRACT Unclassified	c. THIS PAGE Unclassified			19b. TELEPHONE NUMBER (include area code) N/A



CYANATE ESTER GRAPHENE COMPOSITES

29 March 2012

Josiah T. Reams^{1*}, Andrew Guenthner², Kevin R. Lamison³, Joseph M. Mabry²

¹National Research Council / Force Research Laboratory

²Propulsion Directorate, Air Force Research Laboratory

³ERC Incorporated

Ph: 661/275-5664; e-mail: josiah.reams.ctr@edwards.af.mil



Outline



- AFRL Efforts in Cyanate Ester Resins
- Routes to Individual Graphene Sheets
- Graphene Oxidation
- Polycyanurate / GO Composite Prep.
- Preliminary Composite Mechanical and Physical Property Characterization



Acknowledgements:

- National Research Council (NRC) Research Associateship Program (RAP)
- Air Force Office of Scientific Research, Air Force Research Laboratory – Program Support; PWG team members (AFRL/RZSM)



Multi-functional Structural Materials



Objective

Explore the use of graphene-based multi-functional structural materials for added toughness and moisture resistance with minimal loss in strength and stiffness

Methods

Dispersion of individual graphene sheets in polycyanurate resin

- Chemically functionalized graphene
- Graphene oxide

Chemically functionalize graphene sheets with reactive functional groups

- Improved dispersion
- Stronger polymer-filler interface

Characterization

Characterization of chemically functionalized graphene

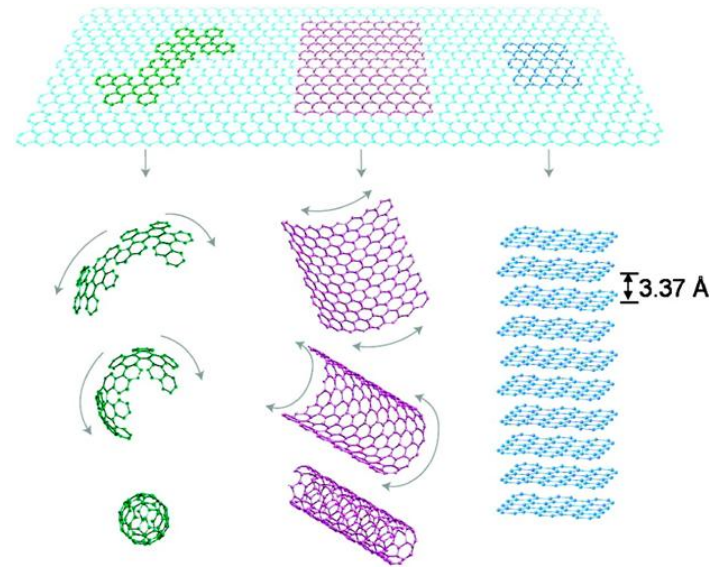
- Type of functional group present
- Degree of functionalization
- Location of reactive groups on surface

Characterization of physical and mechanical properties of graphene composite

- Glass transition temperature
- Stiffness
- Gas and water barrier properties

Benefits

Increased barrier performance and decrease in weight of aerospace composite materials



Reproduced with permission from Kim, H. et. al. *Macromolecules* **2010**, 43, 6515.
Copyright 2010 American Chemical Society.



Potential Applications for Cyanate Ester Resins and Composites



Image courtesy US Navy (public domain)

- Ship structures



Image courtesy NASA (public domain)

- Heat shields



Image by Antonio Pedreira (public domain)

- Microchip housing



U.S. Navy photo by Photographer's Mate
Airman Marvin E. Thompson Jr. (RELEASED)

- Missile Fins, Radomes



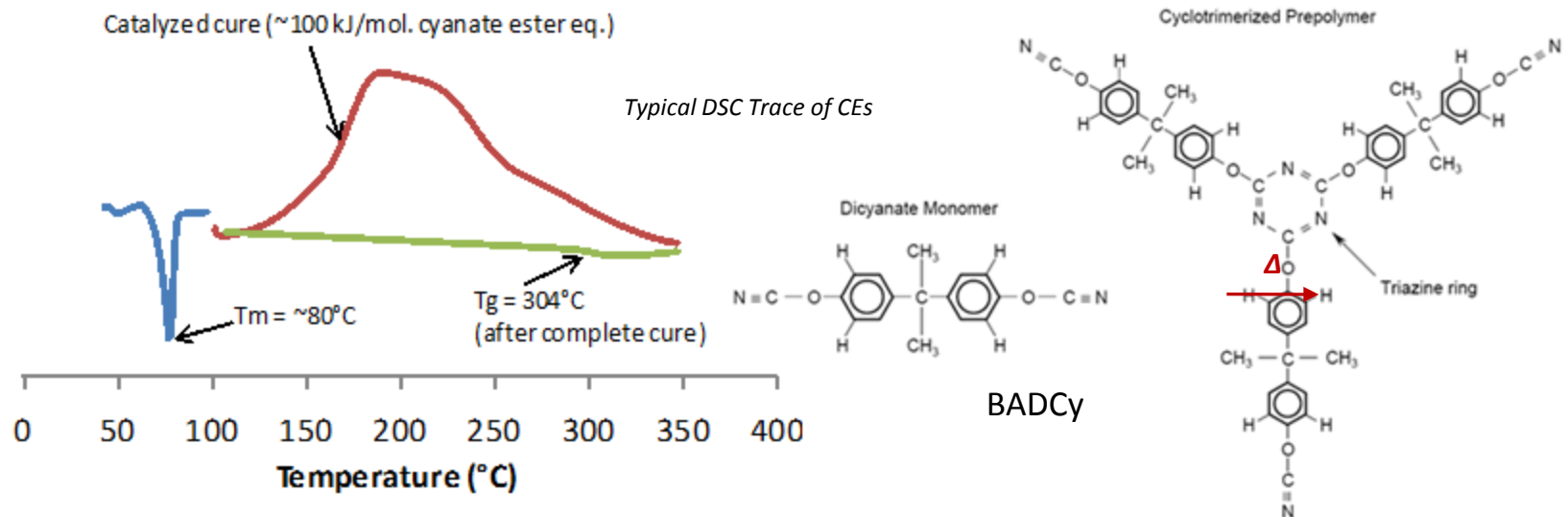
Image courtesy NASA (public domain)

- Spacecraft antennas

- A better understanding of the physical properties, including water uptake, of cyanate ester resins will lead to improved performance in the example applications shown above.



Background: Cyanate Esters



- Glass transition temperatures of $200 - 400^\circ\text{C}$ allow for higher temperature structural components made from continuous fiber-reinforced polymer matrix composites
- Rheological characteristics of cyanate esters compatible with low cost fabrication processes such as RTM and filament winding
- Can be easily compatibilized with tougheners and nanoparticles
- Single species reaction chemistry is “cleaner” than epoxy resin and well-understood; enables development of superior predictive models for failure; readily catalyzed to cure at reasonable temperatures



Importance of Managing Water Uptake



Photo by U.S. Navy photo by
Photographer's Mate 1st
Class Anibal Rivera (public
domain).



- Water can add significantly to launch or take-off weight (3% water in composite resins = about 50 lbs of extra weight on an AV8B)
- Items with high water content can fail catastrophically when suddenly heated
- Long-term exposure to water can facilitate many mechanisms of chemical degradation, necessitating substantial “knock down” factors in design allowables
- Though more stable than epoxy resins, cyanate esters can degrade on long-term exposure to hot water



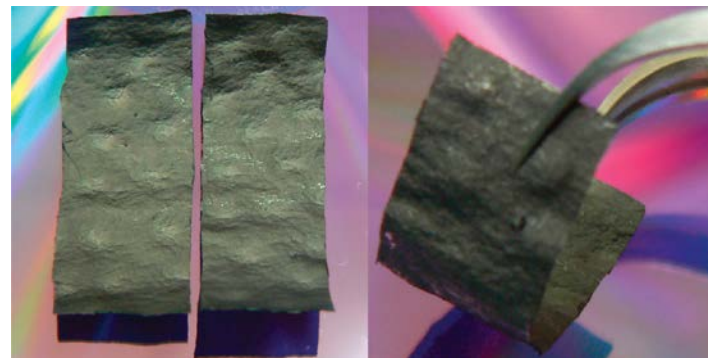
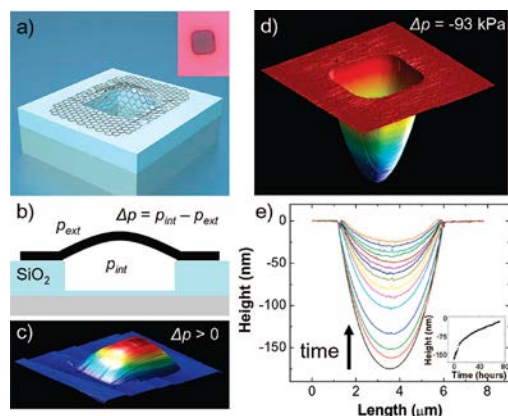
U.S. Navy photo by Photographer's Mate 3rd
Class Mark J. Rebilas (RELEASED)



U.S. Navy photo by Mass Communication Specialist 3rd
Class Torrey W. Lee (public domain)



Background: Graphene



Reproduced with permission from Bunch, S. et. al. *Nano Lett.* **2008**, 8, 2458.
Copyright 2008 American Chemical Society.

Reproduced with permission from Wang, D.W. et. al. *ACS Nano* **2009**, 3, 1745.
Copyright 2009 American Chemical Society.

- Graphene is a 1-atom thick carbon lattice that has been proclaimed as the world's strongest (ultimate strength 130 GPa), and stiffest (Young's modulus 1 TPa) material.^a
- Transport properties: Surface area: 2630 m²/g^b; impermeable to He^c; high thermal conductivity (5000 W/(m·K))^d; high electrical conductivity (6000 S/cm)^e and electron mobility (250,000 cm²/vs at 5K)^f
- In composites, toughness improves with increasing non-bonded surface area while strength and stiffness improve with bonded surface area; the high surface area of graphene allows excellent control over the balance of these properties.
- Graphene is unique in that it can be a reinforcement, barrier, and electrode all at once

a. Lee, C.; Wei, X.; Kysar, J. W.; Hone, J. *Science* **2008**, 321, 385–388.

b. Viculis, L.M.; Mack, J.J.; Mayer, O.M.; Hahn, H.T.; Kaner, R.B. *J. Mater. Chem.* **2005**, 15, 974-978.

c. Bunch, J. S.; Verbridge, S. S.; Alden, J. S.; van der Zande, A. M.; Parpia, J. M.; Craighead, H. G.; McEuen, P. L. *Nano Lett.* **2008**, 8, 2458–2462.

d. Balandin, A. A.; Ghosh, S.; Bao, W.; Calizo, I.; Teweldebrhan, D.; Miao, F.; Lau, C. N. *Nano Lett.* **2008**, 8, 902–907.

e. Du, X.; Skachko, I.; Barker, A.; Andrei, E. Y. *Nature Nanotechnol.* **2008**, 3, 491–495.

f. Service, R.F.; *Science* **2009**, 324, 875-877.



Routes to Individual Graphene Sheets

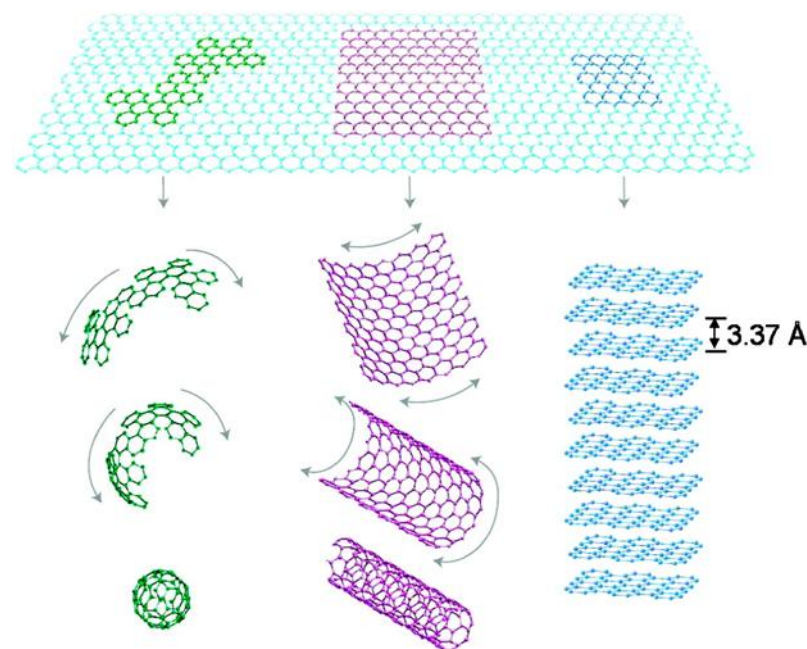


- Bottom-Up Methods

- Chemical Vapor Deposition (CVD)
- Arc Discharge
- Epitaxial Growth
- Good for evaluation of physical and mechanical properties
- Produces small amounts of material

- Top-Down Methods

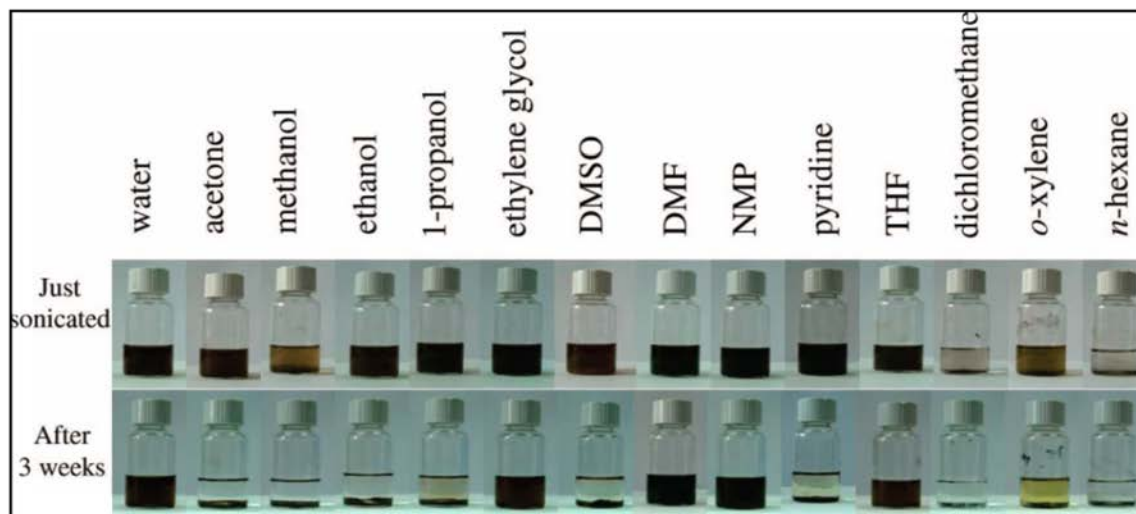
- Micromechanical Cleavage
- Acid Intercalation
- Oxidation of graphite
- Produces relatively large amounts of material
- Often leads to a reduction in attractive properties



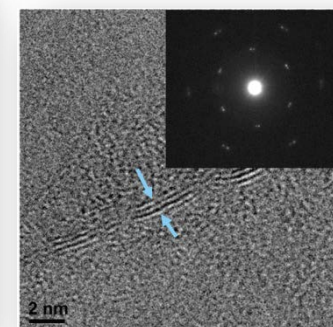
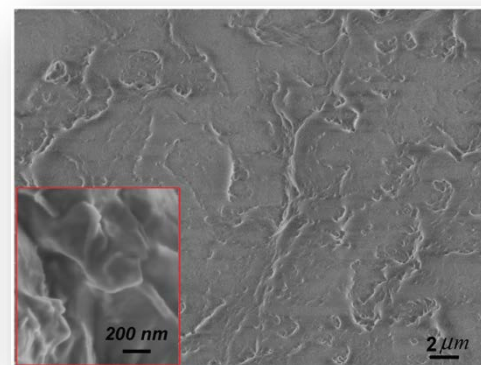
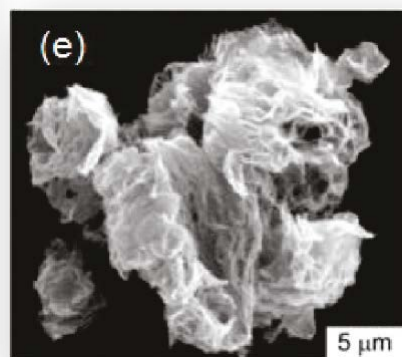
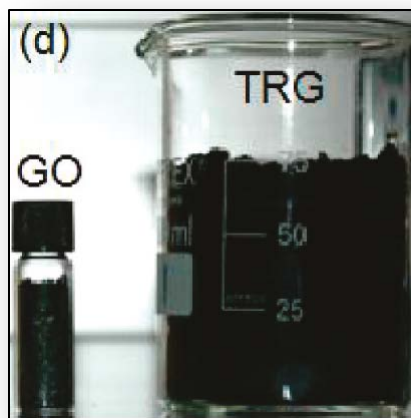
Reproduced with permission from Kim, H. et. al. *Macromolecules* **2010**, 43, 6515.
Copyright 2010 American Chemical Society.



Graphite Oxide



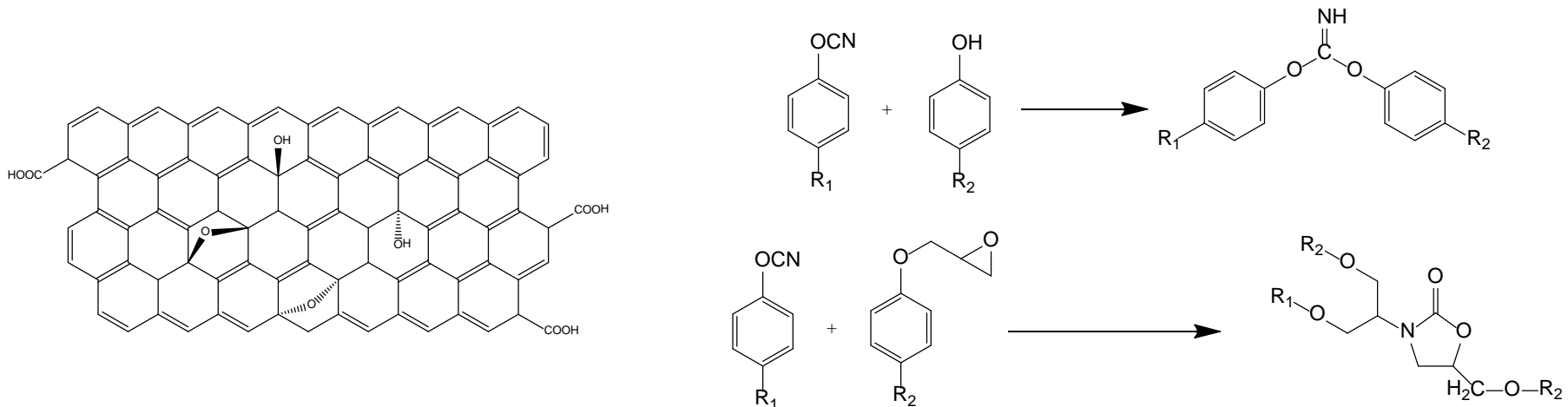
Reproduced with permission from Paredes, J.I. et. al. *Langmuir* **2008**, 24, 10560. Copyright 2008 American Chemical Society.



Reproduced with permission from Kim, H. et. al. *Macromolecules* **2010**, 43, 6515. Copyright 2010 American Chemical Society.



Graphene Oxide Cyanate Ester Composite Potential Reactions



- Chemical oxidation of graphite results in hydroxyl and oxirane functionalities on the surface of individual graphene sheets
He, H. et. al. *Chem. Phys. Lett.* **1998**, 287, 53–56.
- Oxygen functionalities on graphene surface and edges may impart favorable interactions for good dispersion
- Interactions between oxirane and hydroxyl moieties with polycyanurate matrix (both non covalent and covalent) may provide improved physical and mechanical properties
- Careful analysis of the graphene reactant and product will be needed to understand chemical structure and reproduce key properties



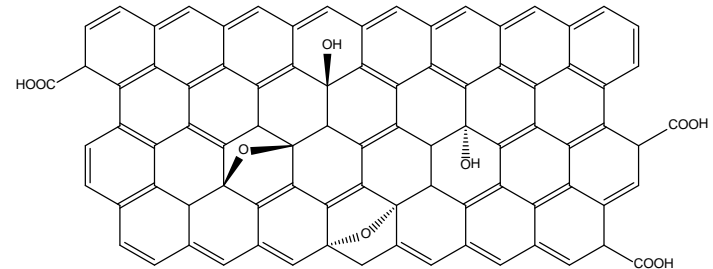
Graphene Oxide LECy Composite Fabrication



- Hummers method of oxidation

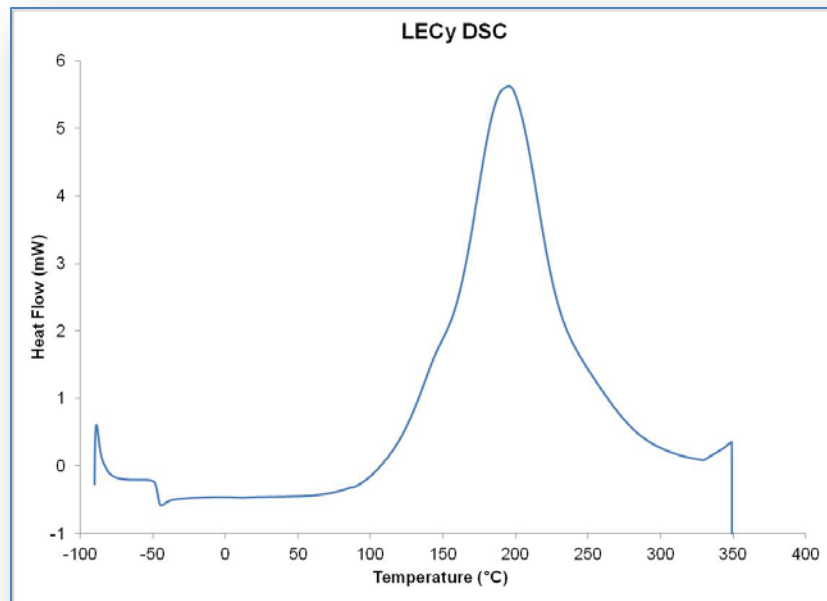
Hummers, W. S., Jr.; Offeman, R. E. *J. Am. Chem. Soc.* **1958**, 80,1339.

- H_2SO_4 , KMnO_4 , NaNO_3
 - H_2O wash
 - Filtration
- Forms stable dispersions in water and polar organic solvents
- Graphene oxide dispersed in LECy / catalyst by high shear mixing (1 hour) followed by sonication (1 hour)
- Catalyst (2phr): 1:30 by weight Cu(II) acetylacetonate : nonylphenol
- Mixture degassed at 300 mm/Hg 30 minutes at 90 °C and prior to pouring into silicone molds
- Cure schedule: 150°C 1hour, 210 °C 24 hours (5 °C/min ramp rate)



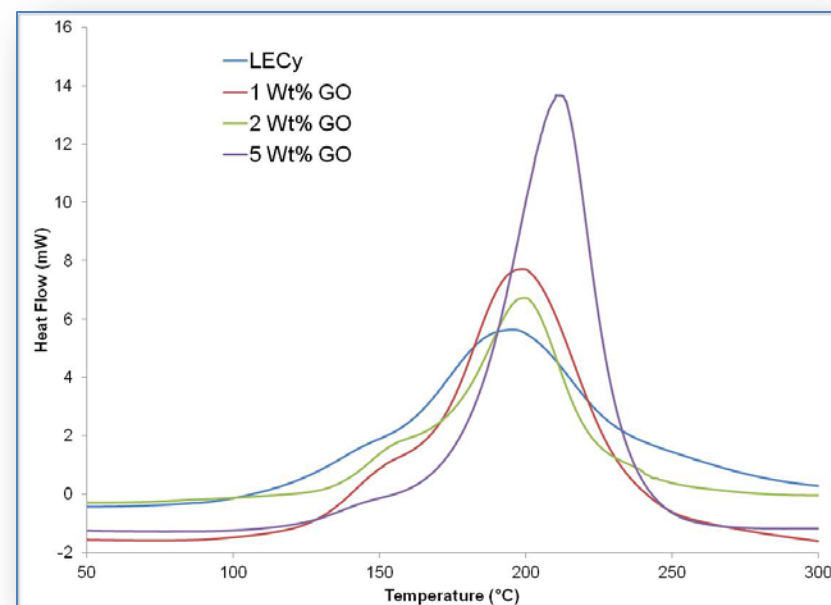


Graphene Oxide Composite Cure



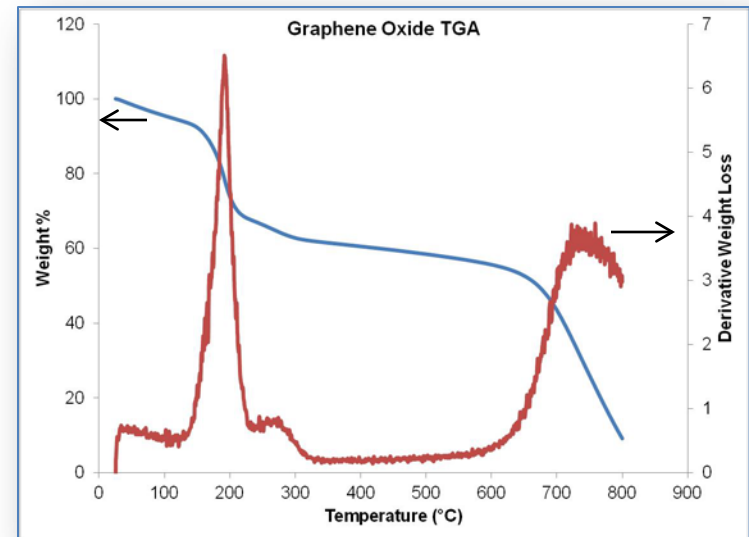
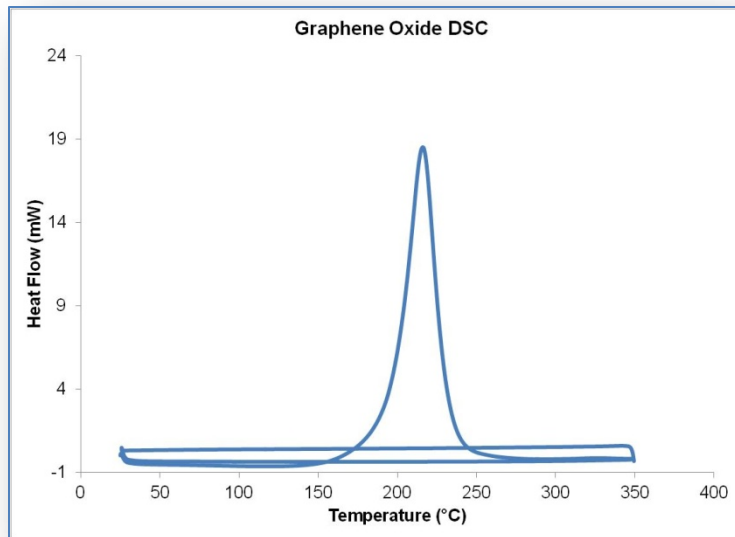
Dispersion of graphene oxide in LECy dicyanate did not significantly change the cure kinetics of the monomer. Therefore, the attractive processing characteristics of LECy are retained in graphene oxide / LECy mixtures.

Impurities, such as aryl phenols and transition metals, catalyze cyclotrimerization and lowers the peak of the cure exotherm temperature thereby narrowing the processing “window.”

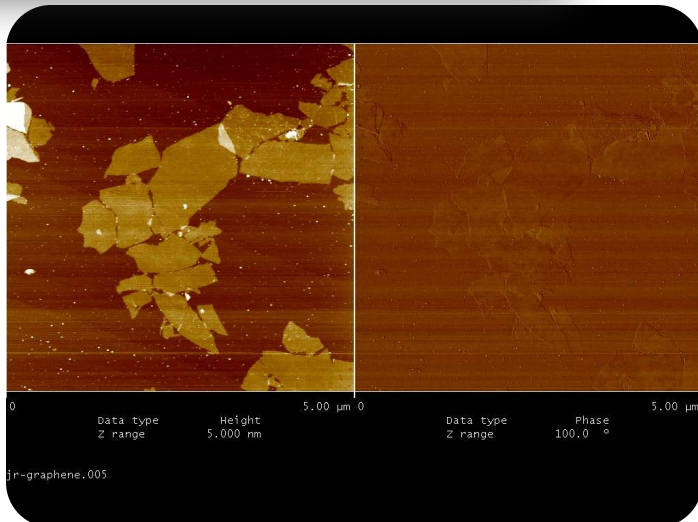




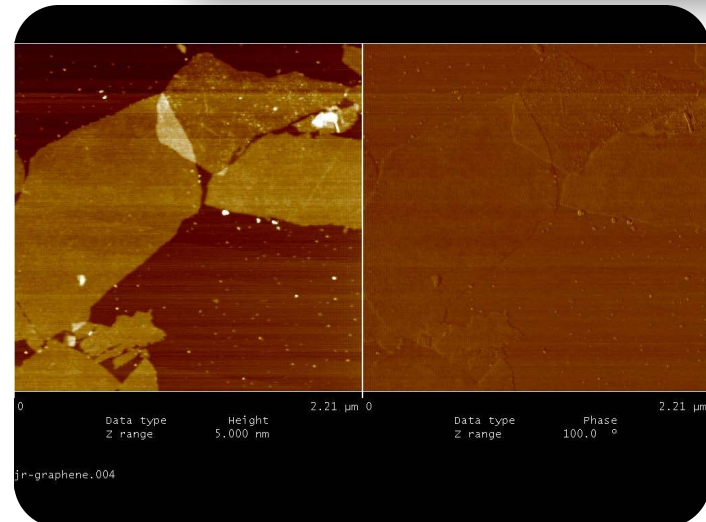
Characterization of Graphene Oxide



AFM image
(5 μm x 5 μm)
of graphene
oxide



AFM image
(2.2 μm x 2.2 μm)
of graphene oxide



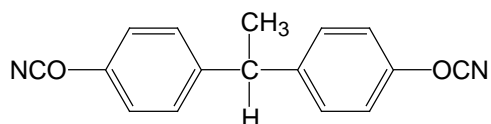


Graphene Oxide Composites: Dynamic Mechanical Analysis (DMA)

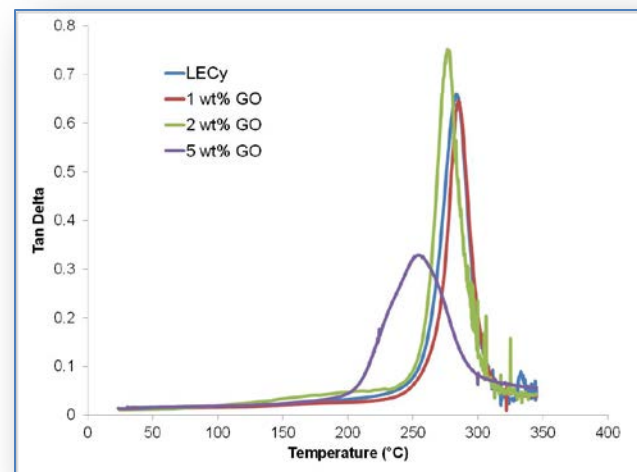
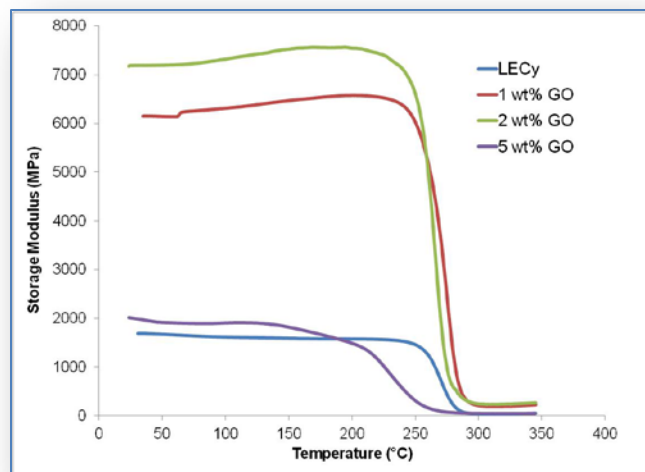
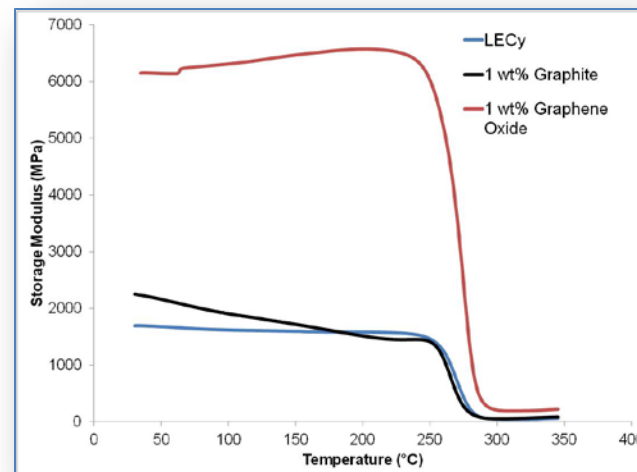


LECy dicyanate (matrix)
purchased from Lonza

- Liquid at room temperature
- Low viscosity

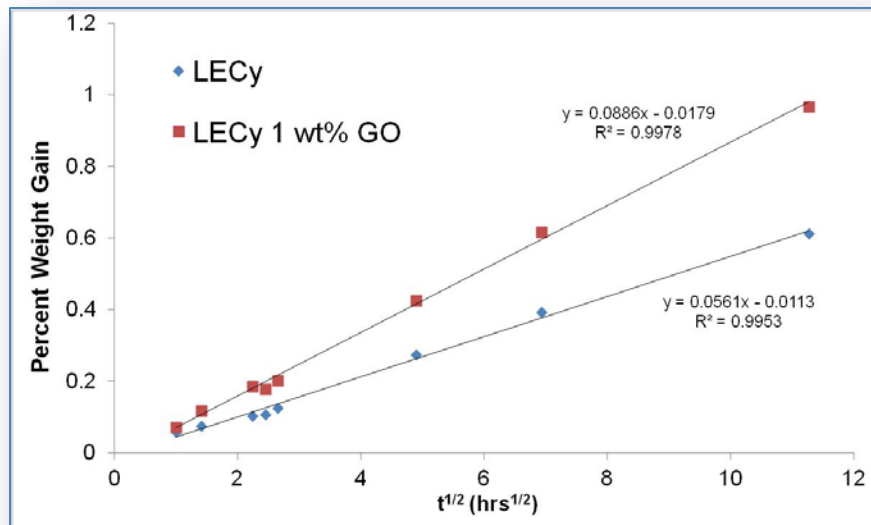


LECy





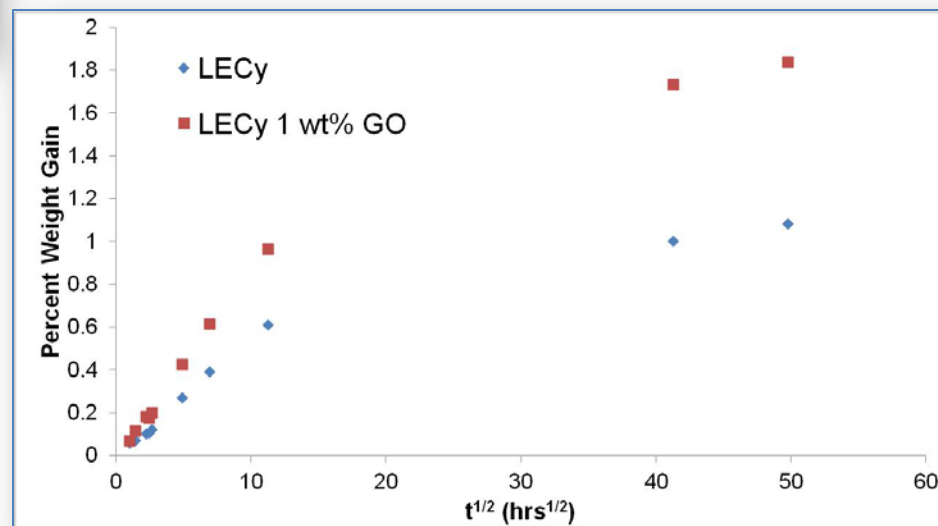
Graphene Oxide Composites: Ambient Temperature Water Uptake



- Rectangular samples with dimensions of approximately 31 mm X 12 mm X 3 mm were immersed in deionized water at ambient temperature
- Equilibrium weight gain of LECy / graphene oxide sample was greater than pure LECy polycyanurate
- Diffusion coefficient of graphene oxide composite sample was less than LECy polycyanurate

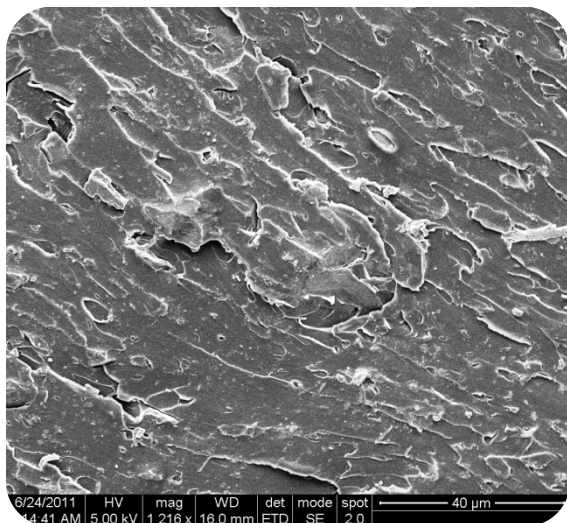
$$D = \frac{\pi}{t} \left(\frac{IM_t}{4M_m} \right)^2 = \pi \left(\frac{I\Theta}{4M_m} \right)^2$$

Sample	M _m (%)	D · 10 ⁻⁸ (cm ² /s)
LECy	1.08	1.21
1 wt% GO	1.84	1.14





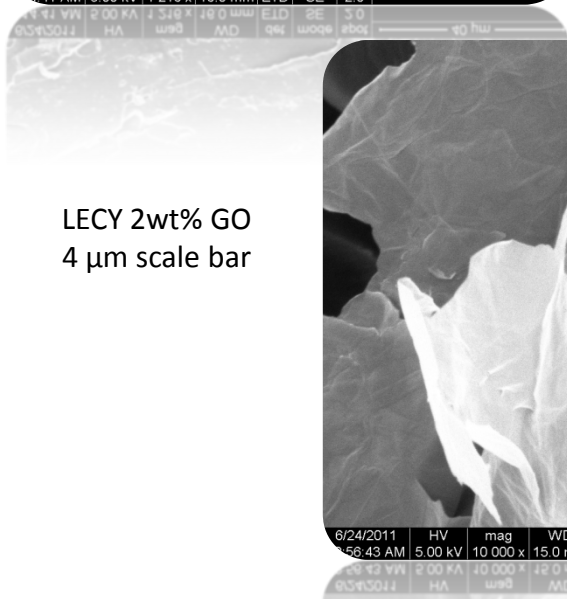
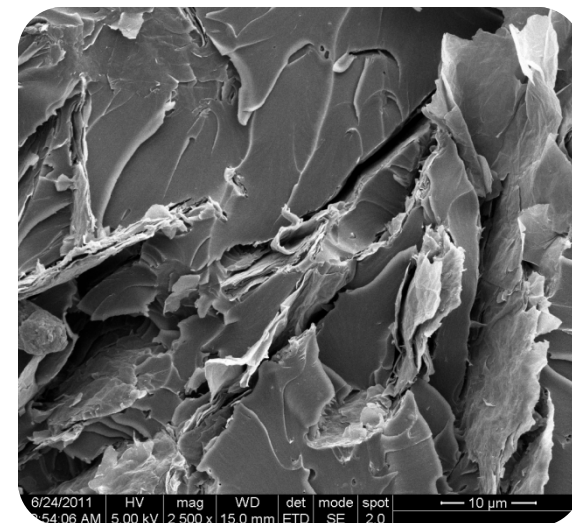
Graphene Oxide Composites: Scanning Electron Microscopy (SEM)



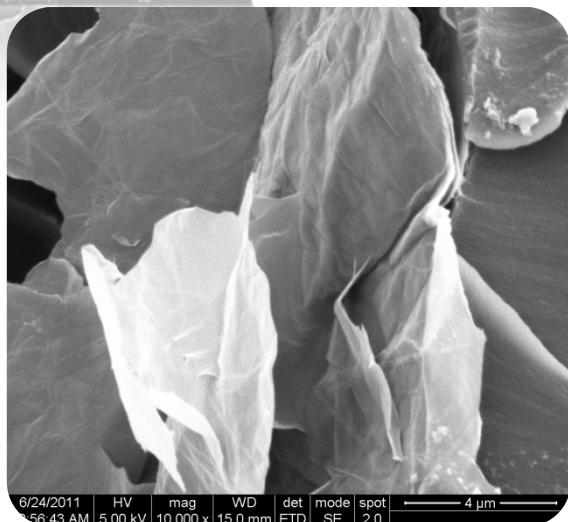
LECY 1wt% GO
40 μm scale bar

LECY 2wt% GO
10 μm scale bar

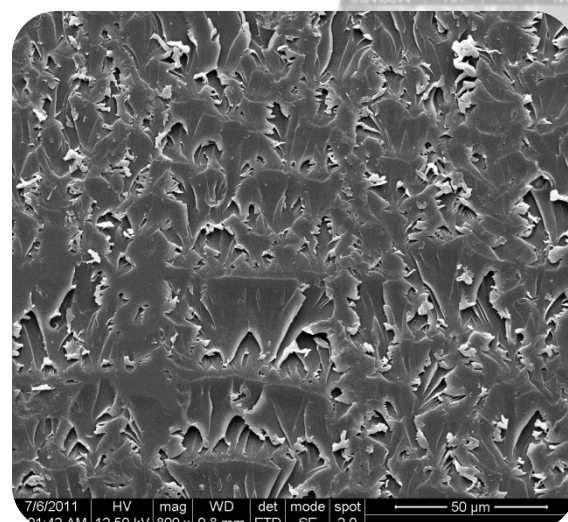
- SEM micrographs suggest that LECy polycyanurate matrix is not covalently bonded to graphene sheets
- Matrix-filler interface is likely dominated by intermolecular forces rather than covalent bonding



LECY 2wt% GO
4 μm scale bar

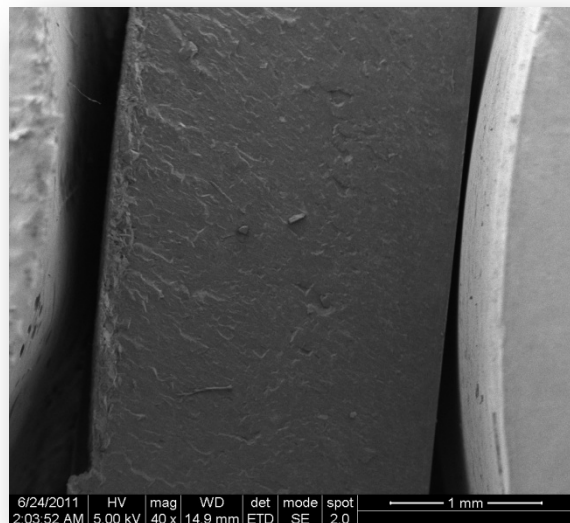


LECY 1wt% GO
50 μm scale bar
microtomed surface





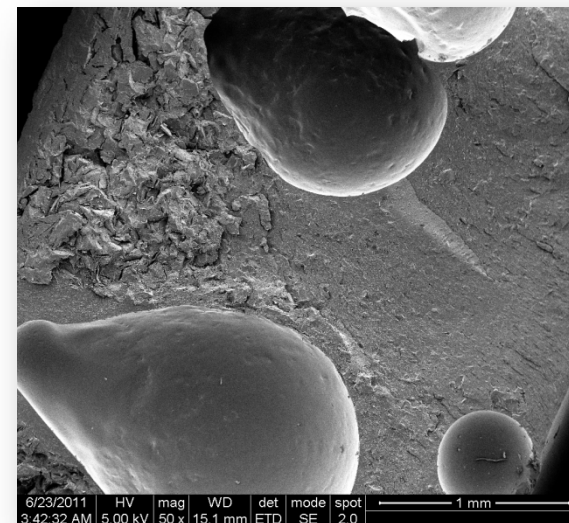
Graphene Oxide Composites: Platelet Dispersion



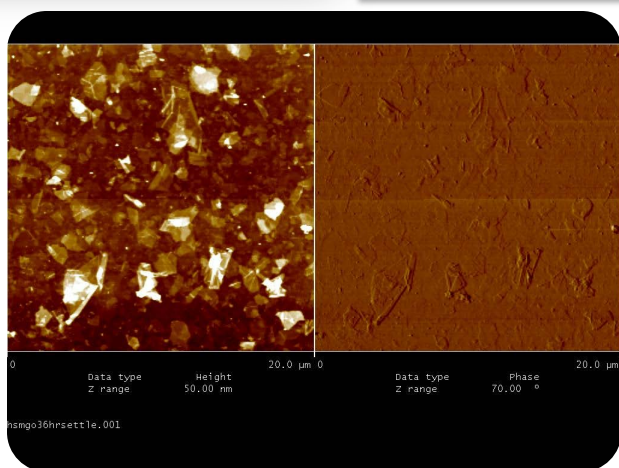
LECY 1wt% GO
1mm scale bar

LECY 5wt% GO
1mm scale bar

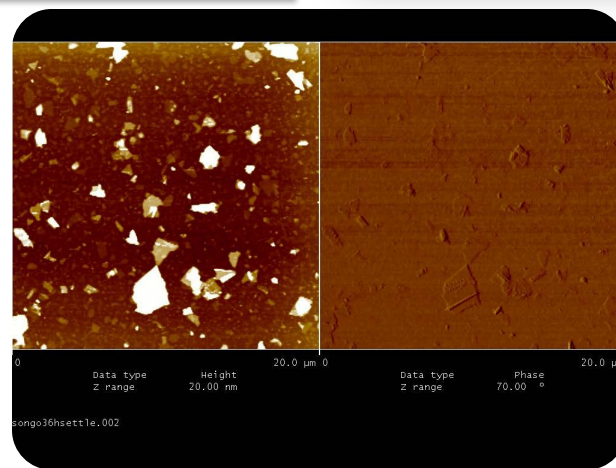
- Void content and settling was low in the LECy 1 wt% GO composite and much greater in the 5 wt% GO sample
- Lateral dimensions of GO sheets were approximately the same for both high shear mixed and sonicated GO



AFM image
(20 μ m x 20 μ m)
high shear mixed
graphene oxide



AFM image
(20 μ m x 20 μ m)
sonicated
graphene oxide





Summary

- Graphene oxide produced by chemical oxidation formed stable dispersions in LECy cyanate ester matrix and edge functionalized graphite does not
- High shear mixing followed by sonication was the best method for graphene oxide dispersion in LECy
- Addition of 1 wt% edge-functionalized graphite to LECy did not increase storage modulus but addition of 1 and 2 wt% Go increased storage modulus below the T_g
- Diffusion of water in LECy 1 wt% GO was slower than pure LECy polycyanurate but equilibrium uptake was greater
- SEM micrographs of composite fractured surfaces suggest that LECy cyanate resin matrix is not covalently bonded to graphene oxide sheets
- LECy 1 wt% GO composite samples showed relatively good dispersion and low void content
- Poor dispersion and large voids were present in LECy 5 wt% composites



AFRL

THE AIR FORCE RESEARCH LABORATORY
LEAD | DISCOVER | DEVELOP | DELIVER

